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Molecular exchange in liquid-vapour system

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In a liquid-vapour system evaporation and condensation take place simultaneously and at thermodynamic equilibrium the exchange of molecules between liquid and vapour phase is constant. The exchange rate can be calculated by theoretical method provided the exchange coefficient σ is known. An experimental system has been designed to study this molecular exchange phenomenon. A mathematical formula has been derived for this system, so that the value of σ can be obtained. Experimental results for mercury are given in this paper. The effect of several factors influencing this phenomenon, have been studied and results obtained are reported. The value of exchange coefficient for mercury obtained by us is 0.04 ± 0.02.

INTRODUCTION

In recent years, the processes of evaporation and condensation have become an important area of study in nuclear power and airospace industries and it is necessary to know the heat transfer properties of various liquid metals used in nuclear power reactors. In practice both evaporation and condensation take place simultaneously (Knacke & Stranski 1956), and hence net mass transfer flux J_{net} is given by

$$J_{net} = J_e - J_c \qquad \ldots (1)$$

where J_e and J_c are the rate of evaporation and condensation, respectively. For thermodynamic equilibrium

$$J_{net} = 0, \quad \text{therefore} \quad J_e = J_c = J$$

and evaporation coefficient σ_e and condensation coefficient σ_c are equal

$$i.e., \; \sigma_e = \sigma_c = \sigma.$$

σ is known as exchange coefficient. However, one is not sure of what is going on at the interphase If there is an evaporation at the interphase then to maintain the thermodynamic equilibrium the condensation rate should be equal to the evaporation rate. This means that an exchange in the molecules of liquid and vapour phase is taking place; this process is known as Molecular Exchange Phenomenon. For such an exchange process one can estimate the values of J provided the value of the exchange coefficient σ can be found by an experimental method such as described in the following sections. In this study mercury has been used as a test material.

Theoretical Analysis

The system used for this analysis is shown in figure 1 and consists of a vaporization chamber of volume V. This chamber contains two mercury holders, one filled with normal untagged mercury Hg(1) and one with radiactive (tagged) mercury Hg(2). The mercury holders are provided with valves which are capable of covering and uncovering the mercury surfaces. The whole system is maintained at a temperature T.

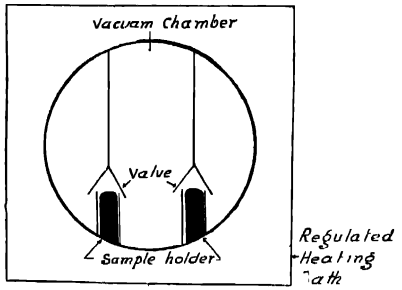

Fig 1 System used for Theoretical Analysis.

Initially both the holders are covered and the vaporization chamber is evacuated. The mercury holder (1) is uncovered for a time interval sufficient to permit the vapour chamber to be filled with saturated vapours of untagged mercury. At time $t = 0$ the holder (2) is uncovered for a time interval t. During this time interval, the molecules of tagged mercury are evaporated into vapour phase and the mixture of the tagged and untagged mercury molecules from vapour phase is condensed on the tagged liquid mercury surface. This mass transfer analysis can be simplified by making the following assumptions.

1) The molecules of untagged mercury which condense on the surface of tagged mercury do not dilute the concentration of tagged liquid mercury. Therefore, the mole fraction of radioactive mercury molecules in the liquid phase $X_1(t)$, does not change during the time of exchange *i.e.*, $X_e(t) = X_1(0)$. This assumption implies that untagged mercury molecules are mixed instanteneously in the radioactive liquid mercury and dilution is negligible, *i.e.*, the mixing process is not diffusion controlled in the liquid phase.

2) Bulk mixing in vapour phase due to the collision of molecules is instantaneous *i.e.*, the mixing is not diffusion controlled in the gaseous phase.

3) The radioactive liquid mercury surface is free from any kind of contamination.

4) The exchange is taking place in the absence of non-condensable gases in the system.

An increase in number of radioactive mercury molecules in the vapour phase during the exchange time interval from t to $t+\mathrm{d}t$ is $\sigma JAX_1(0)\mathrm{d}t$.

A decrease in number of radioactive mercury molecules in the vapour phase during the exchange time interval from t to $t+\mathrm{d}t$ is $\sigma JAX_v(t)\mathrm{d}t$.

A net transfer of radio-active mercury molecules from liquid to vapour phase in volume V during the exchange time interval from t to $t+\mathrm{d}t$ is given by

$$C_v(\infty)V\mathrm{d}X_v(t) = \sigma JA\mathrm{d}t[X_1(0)-X_v(t)] \qquad \ldots \quad (2)$$

where $X_v(t)$ = the mole fraction of the tagged mercury molecules in vapour phase at time t

$C_v(\infty)$ = the concentration of mercury molecules in the saturated vapour phase,

$\mathrm{d}X_v(t)$ = the change in mole fraction of the radioactive mercury molecules in the vapour phase during the exchange time interval from t to $t+\mathrm{d}t$,

A = tagged liquid mercury surface area used for the exchange process.

On integrating equation 2 between the limits

$$0 < t' < t, \quad \text{and} \quad 0 < X_v(t') < X_v(\infty)$$

we obtain

$$\frac{X_v(t)}{X_l(0)} = [1-\exp(t/\tau)] \qquad (3)$$

where

$$\tau = \frac{VC_v(\infty)}{\sigma JA}.$$

The concentration of the radio-active mercury molecules can be measured by counting methods, therefore (3) can be written as

$$R_{\mathrm{CPM}} = \frac{\left(\dfrac{\mathrm{CPU}}{w}\right)_v}{\left(\dfrac{\mathrm{CPM}}{w}\right)_l} = [1-\exp(-t/\tau)] \qquad (4)$$

where $\left(\dfrac{\mathrm{CPM}}{w}\right)_v$ and $\left(\dfrac{\mathrm{CPM}}{w}\right)_l$ are the counts per minute, per unit mass in vapour phase and liquid phase, respectively, at exchange time t. The value of the exchange coefficient can be calculated from the experimental data by using the slope of $\ln[1-R_{\mathrm{CPM}}]$ *vs* t, plot.

Experimental Investigation

The apparatus used for this investigation is the same as described by us earlier (Singhal 1972), except that in this case two mercury holders are used. The untagged and tagged (Hg-203) mercury samples are loaded in the mercury holders and the system is evacuated and heated. Then the flask is disconnected from the vacuum system by a stopcock (SC2) The flask is filled with saturated vapour of untagged mercury by opening the valve for MH1 for sufficient time. Then, the mercury valve for radioactive mercury MH2 is opened for a predetermined time interval to allow the molecular exchange between vapour phase and liquid phase. The mercury vapour is condensed and weighed The radioactivity in the condensed sample is measured From these data value of exchange coefficient is calculated

Results

Shaded portion of figure 2 shows the experimental results The experimental value of the exchange coefficient is found to be 0 04±0 02 for the range of 103°C and 127°C. The following studies were made during this work.

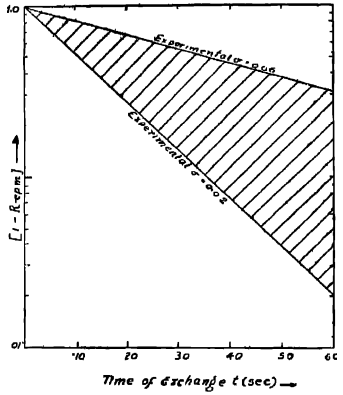

Figure 2 *

1) The effect of temperature on the exchange coefficient was studied by collecting the data for the temperature range of 103°C to 127°C, which lie within experimental limits of this technique. The data indicate that the exchange coefficient is constant for this temperature range.

2) Effect of geometry of the mercury container near the liquid surface was studied and found that it has no effect on the exchange phenomenon.

* Note added in proof In figure 2 the values $\sigma = 0.02$ and $\sigma = 0.06$ should be interchanged.

3) Knudsen's (1915) experience lead us to study the effect of impurity in the mercury samples. The untagged and tagged mercury samples were distilled four times, these samples were loaded in argon atmosphere and the mercury holders were transferred in the system in argon atmosphere. The results did not show any effect on the exchange coefficient, thus the mercury samples used in previous experiments were as good as distilled samples.

4) Since the radioactive mercury is used in the system, the radiations emitted from the sample may ionize the vapour phase and form a cloud of ions around the sample. The radioactive mercury molecules may not move out of this cloud. If this phenomenon exists then the value of the exchange coefficient will be reduced as low as reported in this work. The presence of such phenomenon was studied by using the radioactive mercury of lower activity than used in other experiments. The activity was reduced from $6\ 3 \times 10^4$ CPM/mgm to 300 CPM/mgm. The data obtained for this study indicate that there is no effect of the radioactivity of the mercury sample on the exchange coefficient.

5) The effect of liquid surface area on the exchange phenomena was studied by using a mercury container of smaller opening. The values obtained from these experiments are $\sigma = 0.03 \pm 0\ 02$ for $A = 0\ 045\ \text{cm}^2$ as compared to $\sigma = 0\ 04 \pm 0.02$ for $A = 0.402\ \text{cm}^2$. These values of σ are nearly the same, thus it indicates that the surface area has no effect on the value of the exchange coefficient but it does increase the time of exchange required to establish the equilibrium in the system with decrease of surface area.

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